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Photolysis of 3,4-Dichloroaniline in Natural Waters

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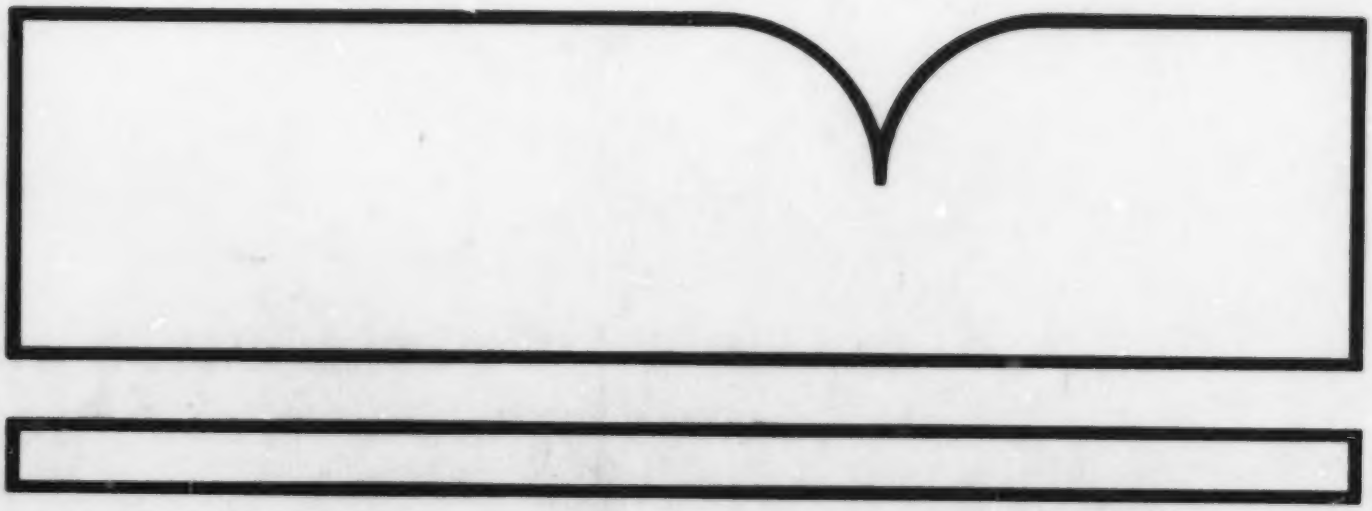

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16. ABSTRACT

Sunlight irradiation of 3,4-dichloroaniline (DCA) in natural water samples resulted in both direct and sensitized photoreactions. A procedure is described for separating the effects of competitive light absorption of the water from sensitized processes. Although the overall photolysis rates of DCA were slower in the natural waters than in distilled water (depth 6.2 cm), the rates in natural waters were faster than expected, on the basis of sunlight received by the DCA. Kinetic results were qualitatively the same when a commercial humic acid solution with similar light absorption characteristics was used. TCAB (3,4,3',4'-tetrachloroacobenzene) was produced in two rice-field waters containing 6.1×10^{-6} to 2.9×10^{-4} M DCA. The concentration of TCAB produced was greater in the more concentrated DCA solutions, although the yields were in no case greater than 1% of the reacted DCA. The chemical yield of TCAB was considerably lower in the commercial humic acid solutions than in the natural water samples. TCAB was not observed in distilled water.

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Photolysis of 3,4-Dichloroaniline in Natural Waters

Glenn C. Miller,* Richard Zisook, and Richard Zepp

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Journal Article

Sunlight irradiation of 3,4-dichloroaniline (DCA) in natural water samples resulted in both direct and sensitized photoreactions. A procedure is described for separating the effects of competitive light absorption of the water from sensitized processes. Although the overall photolysis rates of DCA were slower in the natural waters than in distilled water (depth 6.2 cm), the rates in natural waters were faster than expected, on the basis of sunlight received by the DCA. Kinetic results were qualitatively the same when a commercial humic acid solution with similar light absorption characteristics was used. TCAB (3,4,3′,4′-tetrachloroazobenzene) was produced in two rice-field waters containing 6.1×10^{-6} to 2.9×10^{-4} M DCA. The concentration of TCAB produced was greater in the more concentrated DCA solutions, although the yields were in no case greater than 1% of the reacted DCA. The chemical yield of TCAB was considerably lower in the commercial humic acid solutions than in the natural water samples. TCAB was not observed in distilled water.

INTRODUCTION

3,4-Dichloroaniline (DCA) is an hydrolysis product of several herbicides, notably diuron, linuron, and propanil. As such it has been used in several studies as a model compound to gain basic information on metabolic processes in soils, plants, and animals. Its photochemical fate has also been investigated in four separate studies (Plimmer and Kearney, 1969; Rosen et al., 1970; Moilanen and Crosby, 1972; Mansour et al., 1975). Each study reported 3,4,3′,4′-tetrachloroazobenzene (TCAB) to be a photoproduct in water. This compound is of major interest because it has structural and toxicological similarities to TCDD in that it has produced chloracne in workers in chemical plants producing DCA and is a potent inducer of aryl hydrocarbon hydroxylase in chick embryos (Poland et al., 1976).

Previous work (Miller et al., 1979) has shown that the major direct protolysis product of DCA in distilled water is 2-chloro-5-aminophenol (>78% conversion) (Figure 1). The reaction is suggested to proceed through an aryl cation intermediate that reacts with any available nucleophile, generally water. A minor photoreduction product, 3-chloroaniline, was also observed. This appears to be a singlet-state reaction and thus is probably not sensitized by triplet-energy transfer under most environmental conditions. However, other indirect processes are possible, as evidenced by the formation of TCAB, particularly when model photosensitizers such as benzophenone (Plimmer and Kearney, 1969) and riboflavin (Rosen et al., 1970) are present. These model compounds may or may not produce results applicable to an agricultural environment.

Substances in natural waters are also known to sensitize the photodegradation of xenobiotics by several indirect processes. They may be caused by hydrogen abstraction; by oxidation with superoxide, hydrogen peroxide, hydroxyl radicals or singlet oxygen; or by reaction with other photochemically generated intermediates. Our investigation sought to answer two questions: first, do the dissolved substances in natural waters sensitize the photolysis of DCA, and second, do they promote the formation of TCAB.

EXPERIMENTAL PROCEDURES

Materials and Equipment. Natural water samples were obtained from three rice fields and the Sacramento River near Davis, CA, and a Lovelock, NV, alfalfa irrigation ditch. Each was passed through Whatman No. 40 filter paper prior to use. Humic acid (Fluka AG) was obtained from Columbia Organic Chemicals Co. A stock solution was made by adding solid humic acid to tap water, followed by filtering the undissolved material. The resulting solution was diluted to give the attenuations shown in Table II.

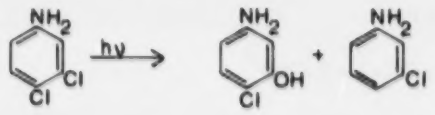
DCA was obtained from Aldrich Chemical Co. and recrystallized three times from 95% EtOH (mp 72 °C). TCAB was synthesized by the method of Corbett and Holt (1963).

DCA and TCAB were determined on a Varian 1700 gas chromatograph equipped with a ^{3}H electron capture detector and a 1 m length × 2.1 mm i.d. nickel alloy column containing 2% OV-210- 2% OV-17 on 100/120 Gas Chrom Q. The oven temperatures for DCA and TCAB were 175 and 225 °C, respectively. Further evidence for the identity of TCAB was obtained by cochromatography of the suspect peak with an authentic standard on a 0.7 m × 2.1 mm i.d. glass column containing 2% OV-101, employing a nitrogen phosphorus detector. The lack of close eluting peaks, response to two specific detectors, and cochromatography on the two columns of differing polarity confirmed the presence of TCAB. Ultraviolet spectra (Figure 2) were obtained on a Beckman Model 25 spectrophotometer.

Procedures. All of the studies were performed outdoors in sunlight. Solutions of DCA were set outdoors in uncovered Pyrex dishes (6.2 cm deep × 12 cm in diameter). The sides of the dishes were covered with aluminum foil and the bottoms with black tape. The concentration of DCA was adjusted so that the absorbance through 6.2 cm of water was less then 0.1 at 300 nm. One milliliter of saturated DCA was added to 1 L of each water, giving a DCA concentration of 3.0×10^{-6} M. Samples were taken at appropriate time intervals and stored in the dark until analyzed. DCA was determined by partitioning the DCA into an equal volume of benzene followed by injection of aliquots of the organic layer into the gas chromatograph. Quantitation was by comparison of peak height with standards. Rate constants were obtained by using the integrated first-order rate expression and a least-squares analysis of data.

The TCAB studies were performed by adding saturated aqueous DCA either to distilled water or to humic acid solutions; in the case of the natural waters, solid DCA was added to the water and stirred until completely dissolved. Twenty-five-milliliter aliquots were added to 50-mL volumetric flasks and these were set in the sun. Following

Division of Biochemistry, University of Nevada, Reno, Reno, Nevada 89557 (G.C.M. and R. Zizook), and Environmental Research Laboratory, U.S. Environmental Protection Agency, Athens, Georgia, 30613 (R. Zepp).



DCA

Figure 1. Direct photolysis products of DCA in water (Miller et al., 1979).

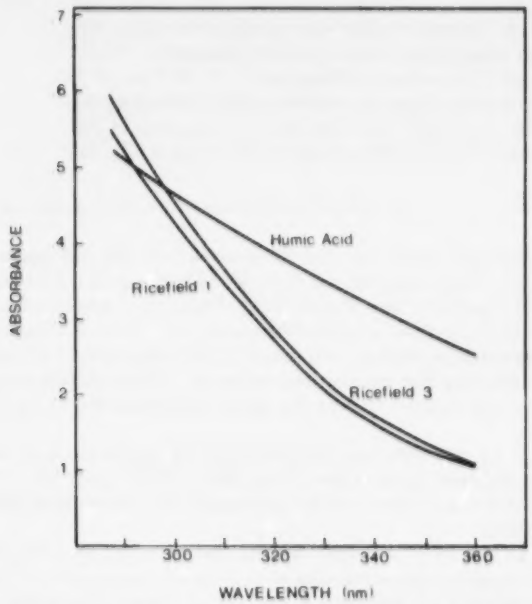


Figure 2. Ultaviolet spectra of waters used in the TCAB experiments. The humic acid spectrum corresponds to the solution having an absorbance of 0.42 (1-cm pathlength) at 317 nm (Table IV). The humic acid solution active in promoting TCAB formation was five times more concentrated.

5 h of midday exposure in May, the flasks were brought into the laboratory; 2 mL was taken for DCA analysis and 2 mL of isooctane was added to the remaining 23 mL. The volumetric flask was shaken, and aliquots of the organic layer were injected on the gas chromatograph as described above. Concentrations were determined by comparison of peak heights with TCAB standards. Dark controls showed no reaction in all cases.

RESULTS AND DISCUSSION

Sensitization. Two factors must be considered when examining the importance of photosensitized processes in natural waters: the rate of competitive transformation by direct photolysis and light attenuation by the substances in the water.

In distilled water direct photolysis is the only mechanism for photo-transformation. The direct photolysis rate can be computed by using eq 1 where $-d[DCA]/dt$ is the

$$\frac{-d[DCA]}{dt} = \phi k_a[DCA] \qquad (1)$$

photolysis rate of DCA, ϕ is the reaction quantum yield, 0.052 (Miller et. al., 1979), and $k_a[DCA]$ is the average rate of light absorption of DCA over all wavelengths of sunlight. When the above equation and the solar computer program of Zepp and Cline (1977) are used, the variation in midday direct photolysis half-life can be determined (Figure 3). As can be seen, the annual variation in direct photolysis is substantial, varying with the short-wavelength ultraviolet component of sunlight.

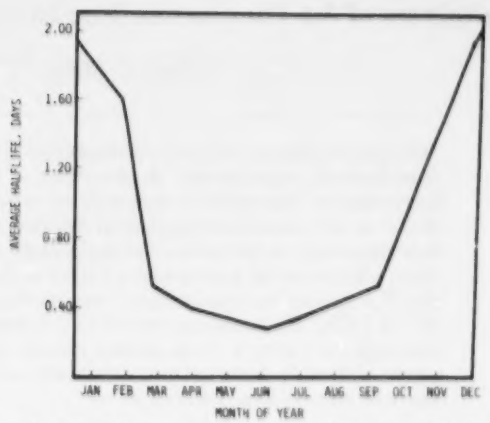


Figure 3. Calculated seasonal variation of direct photolysis rate constants of DCA, latitude 40° N, clear water.

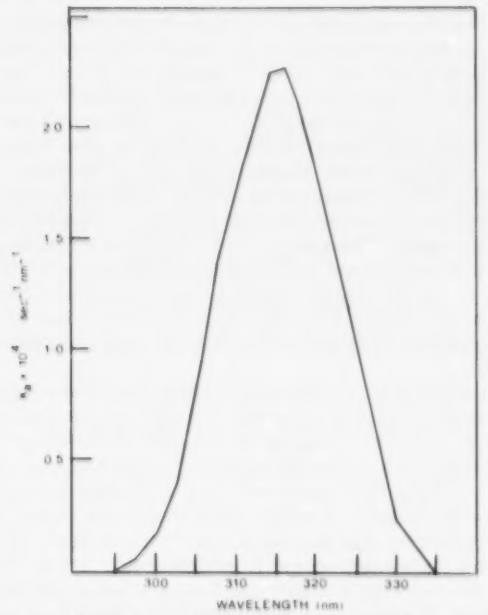


Figure 4. Absorption of solar radiation by DCA at midday, midsummer, latitude 40° N.

The influence of light attenuation has been considered previously (Zepp and Cline, 1977; Miller and Zepp, 1979a). The specific rate of light absorption k_a is proportional to light intensity. The reduction in light intensity vs. depths is calculated by eq 2, where $I(z,\lambda)$ is the irradiance at

$$I(z,\lambda) = W_\lambda e^{-Kz} \qquad (2)$$

wavelength λ and depth z, W_λ is the irradiance immediately below the surface of the water body, and K is the diffuse attenuation coefficient at wavelength λ. For these studies K was estimated by multiplying the decadic absorption coefficient of the solution at 317 nm by 2.3 and by the "distribution function". A distribution function of 1.1 was used because geometry of the Pyrex dishes favors vertical penetration of sunlight compared to that in open water bodies (1.19 times the depth) (Zepp and Cline, 1977). In order to simplify the calculation, the mean attenuation coefficient was used instead of coefficients at each wavelength. The mean wavelength was determined as described (Miller and Zepp, 1979a) by analysis of the wavelength dependence of the specific sunlight absorption rate of DCA at midsummer. The number of photons absorbed above

Table I. Sensitizing Factors for DCA Photolysis in Natural Waters

	$K_{317\ nm}$[a]	$(k_{nw}/k_{dist})_{obsd}$[b]	$(k_{nw}/k_{dist})_{pred}$[c]	S[d]
rice field 1	0.71	0.64	0.22	2.9
rice field 2	0.32	0.53	0.43	1.3
rice field 3	0.76	0.75	0.19	3.9
Sacramento River	0.74	0.76	0.21	3.6
Nevada drainage	0.32	0.60	0.44	1.4

[a] Diffuse attenuation coefficients were computed by multiplying absorbance (1-cm pathlength) of the natural water by 2.303 and by the distribution function (1.1). [b] Ratio of photolysis rate constants observed in natural water samples and distilled water. [c] Ratio of rate constants are affected only by light penetration. [d] Computed using eq 4.

317 nm is equivalent to that absorbed below 317 nm (Figure 4).

The average radiation (I_{av}) received by a pollutant is the space average of radiation in the water column (Miller and Zepp, 1979a) (eq 3.) Because the photolysis rate of a

$$I_{av} = W\frac{(1 - e^{-Kz})}{Kz} \tag{3}$$

pollutant is directly dependent on light intensity, a reduction in I_{av} through light attenuation would produce a proportional decrease in direct photolysis rate if no indirect processes were involved. In distilled water sunlight is attenuated much less than in most inland surface waters, and, at depth of 10 cm or less, I_{av} approximately equals W. It follows that the predicted ratio of the photolysis rate constants in a natural water sample to that in distilled water $(k_{nw}/k_{dw})_{pred}$ should equal $(1 - e^{-Kz})/Kz$ if the natural substances affect photolysis only by light attenuation. This ratio is observed experimentally only if (1) the pollutant concentration is sufficiently low that it has a negligible effect on light attenuation (2) the reaction quantum yield for direct photolysis is unaffected by the natural substances in the water, and (3) indirect processes (photosensitized reactions) are not involved. In this paper we have determined "sensitization factors" S for photolysis of DCA in several natural water samples (eq 4, where $(k_{nw}/k_{dw})_{obsd}$ is the ratio of photolysis rate constants observed in natural and distilled water, respectively). This

$$S = \frac{(k_{nw}/k_{dw})_{obsd}}{(k_{nw}/k_{dw})_{pred}} = \frac{(k_{nw}/k_{dw})_{obsd}Kz}{1 - e^{-Kz}} \tag{4}$$

ratio relates the predicted photolysis rate based on light attenuation to that determined experimentally. If S equals 1, no sensitization is involved. If different than 1, processes other than direct photolysis are occurring.

Sensitization of DCA photolysis was investigated in five natural waters. Each was obtained from an area expected to receive agricultural runoff or, in the case of the rice fields, direct application of pesticides. The attenuation coefficients of the waters (317 nm) varied from 0.32 to 0.76 cm^{-1} (Table I). The waters with higher attenuation coefficients also appeared darker visually. In all cases the overall photolysis rates were reduced compared to distilled water. When light attenuation was considered, however, sensitization was observed in all cases, again with a rough correlation to the attenuation coefficient. The higher the attenuation coefficient, the greater the sensitization factor.

Because "natural waters" are at best poorly defined and highly variable, water containing a commercial humic acid was used in an attempt to model natural waters with an easily controlled material. As can be seen from Table II, the results obtained are qualitatively the same. That is, the higher the humic acid absorption, the higher the sensitization factor. This humic acid was, however, somewhat less active than the dissolved substances in the natural waters.

Table II. Sensitizing Factors for DCA Photolysis in Humic Acid Solutions[a]

	$K_{317\ nm}$	$(k_{nw}/k_{dist})_{obsd}$	$(k_{nw}/k_{dist})_{pred}$	S
Fluka humic acid (1)	0.32	0.57	0.43	1.3
Fluka humic acid (2)	0.64	0.55	0.25	2.2
Fluka humic acid (3)	1.28	0.42	0.12	3.5

[a] See footnote in Table I.

Table III. TCAB Formation in Sunlight-Irradiated Natural Waters Containing DCA

water	[DCA], M (initial)	% degraded	[TCAB], M
rice field 1	2.9×10^{-4}	48	8.6×10^{-5}
	6.3×10^{-5}	>90	7.2×10^{-5}
	6.3×10^{-6}	>90	0.5×10^{-6}
rice field 3	3.6×10^{-4}	58	47×10^{-6}
	6.1×10^{-5}	>90	23×10^{-6}
	6.1×10^{-6}	>90	0.8×10^{-6}
distilled water	5.5×10^{-4}	71	$<0.1 \times 10^{-6}$
	5.7×10^{-5}	>90	$<0.1 \times 10^{-6}$
	5.7×10^{-6}	>90	$<0.1 \times 10^{-6}$

Table IV. TCAB Formation in Sunlight-Irradiated Humic Acid Solutions Containing DCA

absorbance[a] (317 nm)	[DCA], M (initial)	% degraded	[TCAB], M
0[b]	6.4×10^{-5}	>90	$<0.2 \times 10^{-6}$
	7.3×10^{-6}	78	$<0.2 \times 10^{-6}$
0.42	6.4×10^{-5}	79	$<0.2 \times 10^{-6}$
	6.9×10^{-6}	61	$<0.2 \times 10^{-6}$
2.0	6.6×10^{-5}	71	$<0.2 \times 10^{-6}$
	6.8×10^{-6}	41	0.6×10^{-6}

[a] The absorbances (1-cm path length) were taken in the absence of DCA. [b] Distilled water.

TCAB Formation. The previous reports of DCA photooxidation to TCAB used benzophenone and riboflavin as sensitizers. The triplet energies of these chemicals are 69 (Turro, 1965) and 47.3 kcal/mol (Song and Moore, 1968), respectively. Although the triplet energy of DCA has not been measured, it is probably not less than 73 kcal/mol since the triplet energy of aniline is 77 kcal/mol (Turro, 1965) and chlorines do not lower triplet energies more than 2 kcal/mol for each chlorine (see, for example, Cowan and Drisko, 1976). Hence, the process whereby TCAB is formed by using either of the above sensitizers is most likely through hydrogen abstraction by the sensitizer. Indeed, such a mechanism has been suggested by Bartholomew et al. (1971) for the photosensitized oxidation of aniline. Benzophenone (Turro, 1965), particularly, is known to be an efficient excited-state hydrogen abstractor and has been shown to photosensitize the oxidation of aniline to azobenzene (Santhanum and Ramakrishnan, 1970).

DCA was exposed to sunlight at three concentrations in two rice field waters (Table III) and a water containing humic acid (Table IV), to determine whether natural photosensitizers (Figure 4) similarly promote the formation of TCAB. The concentration of DCA was low enough at the two lower concentrations to not affect the sunlight penetration into the water. The highest concentration of DCA in each water did absorb a significant percentage of sunlight, and thus the percentage loss of DCA was significantly reduced.

Both rice-field waters were active in producing TCAB, at all concentrations tested. As would be expected with a reaction involving dimerization, the higher the initial DCA concentration, the greater the TCAB formation. However, no direct correlation of TCAB produced vs. initial DCA concentration was observed, probably due to several factors. Competitive absorption and direct photolysis of DCA, oxygen content, and pathways other than TCAB formation affect the TCAB yield. Even at the highest conversion of DCA to TCAB, it accounted for less than 1% of the reacted DCA.

Significantly, TCAB was not observed ($<0.1 \times 10^{-8}$ M) in any of the distilled water samples, indicating that direct photolysis processes do not appear to result in TCAB formation. Additionally, the highest concentration distilled water solution was only slightly colored at the termination of the experiment. Both highest concentration irradiated rice-field waters were dark brown, evidence of extensive oxidative polymerization. At the lowest DCA concentrations, the rice field waters had less coloration at the termination of the experiment than the controls, indicating that the rice field waters only promoted the coloration and were not solely responsible for the color.

Solutions of Fluka humic acid (Table IV) were significantly less active than the natural waters in producting TCAB. Only the most concentrated humic acid solution (absorbance 2.0 at 317 nm) with the highest concentration of DCA produced TCAB at concentrations significantly different from the controls. This failure of the humic acids to mimic the TCAB production in the rice-field waters was unexpected since similar kinetic sensitizations were observed in both systems. This is probably due to trapping of the reactive DCA intermediates by the humic acid.

CONCLUSION

These studies describe a method for assessing photosensitized processes in natural waters which involves disentangling competitive absorption from indirect processes. The approach used is similar to that for determining the photoreactivity of nonpolar compounds sorbed on suspended sediments (Miller and Zepp, 1979b). The photolysis rate of DCA was found to be greater than that predicted on the basis of competitive light absorption by the natural waters. The sensitization factors determined for DCA were roughly proportional to the attenuation coefficients of the waters.

Photosensitized formation of TCAB in two rice-field waters was observed, a reaction not found in irradiated, distilled water containing DCA. The reaction mechanism probably involves hydrogen abstraction by materials in the water, followed by recombination and oxidation to give TCAB. This work also demonstrates the value of considering indirect processes initiated by naturally occurring substances when assessing the photolysis of pollutants in water. Not only the rates change, but also the photoproducts. In this case TCAB was formed in the natural water but was not observed as a photoproduct in distilled water.

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